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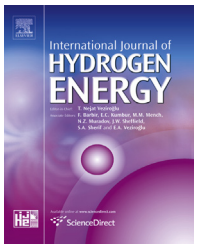

Hierarchical porous carbon catalyst for simultaneous preparation of hydrogen and fibrous carbon by catalytic methane decomposition

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ABSTRACT

Direct coal liquefaction residue was used as the precursor for preparing hierarchical micro-/macro-mesoporous carbon by KOH activation with addition of Al_2O_3, and the resultant carbon AlRC was used as the catalyst for catalytic methane decomposition. The results indicate that the carbon AlRC shows excellent methane conversion, up to 61% after 10 h. Besides hydrogen production from methane decomposition, fibrous carbons were formed on the AlRC catalyst, which is different from other carbon catalysts. The investigations of the formation and growth of the fibrous carbon on the carbon catalyst and its catalytic performance indicated that the formed fibrous carbon contribute to the high methane conversion of AlRC catalyst.

1. Introduction

Compared with the conventional hydrogen production process, such as steam methane reforming, catalytic methane decomposition (CMD) is considered to be one of the most promising methods in the short term owing to no by-products of CO and CO_2, eliminating the need for water gas shift and CO_2 removal stages [1–3]. Meanwhile, the produced carbons from CMD as the main by-product, especially fibrous carbons can be commercialized, thus reducing the net cost of hydrogen production. Both metal-based [3–7] and carbonaceous catalysts [1,2,8–10] can be used for hydrogen production by CMD. Compared with carbon catalysts, metal catalysts are operated at lower reaction temperature and fibrous carbons can be obtained by CMD. However, the utilization of metal catalysts faces some challenges, such as high cost but low stability against deactivation. Moreover, the obtained fibrous carbons on the metal catalysts often have to be further purified by acid treatment before use because of the residual metal particles at the tip of the fibrous carbons. Therefore, various carbon catalysts are gaining increasing attention for CMD.

More than 30 different carbon materials have been tested for the CMD reaction by Muradov [1,2], and the results indicate that activated carbon shows the highest initial catalytic activities while carbon black has the strongest resistance to deactivation. Serrano et al. [11] reported for the first time that ordered mesoporous carbons CMK-3 and CMK-5 have higher and more stable activity than commercial activated carbon and carbon black catalysts. However, the poor activities of traditional carbon catalysts and the expensive template of ordered mesoporous carbons leave much to be desired.

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Besides, up to now, little work has been reported that fibrous carbon can be obtained on carbon catalysts by CMD.

Our previous work reported a simple and effective method for preparing hierarchical porous carbon (HPC) from direct coal liquefaction residue (CLR) by KOH activation with addition of some silica or silicate [12]. Because the additional mineral salts or those formed by the reaction of the additive and KOH can serve as space fillers of nanopores in the thermoplastic CLR, HPCs can be formed by washing off the mineral matters that occupied the inner space of the carbonized sample. Herein, based on the fact that Al_2O_3 is similar to SiO_2 as an amphoteric oxide, hierarchical micro-/macro-mesoporous carbon was prepared from CLR by KOH activation with addition of Al_2O_3 and the resultant carbon was determined as catalyst for CMD. The pore structure of the resultant carbon, the catalytic performance for CMD, and morphology of carbon deposits produced by CMD were investigated. Excellent methane conversion, up to 61% after 10 h, can be obtained on the resultant HPC catalyst, and also it is the first time to report the formation of fibrous carbons by CMD on carbon catalysts. In addition, the formation and growth mechanism of the fibrous carbons was explored on the HPC catalyst.

2. Experimental

2.1. Sample and chemicals

Shenhua CLR was used as the carbon precursor, which was crushed and sieved to particle size of 150–250 μm before use. The proximate and ultimate analyses and the devolatilization behavior of the CLR have been described elsewhere [13]. KOH (Shantou Xilong Chemical Technology Co., China) was used as the activating agent. Commercial Al_2O_3 (the particle size of

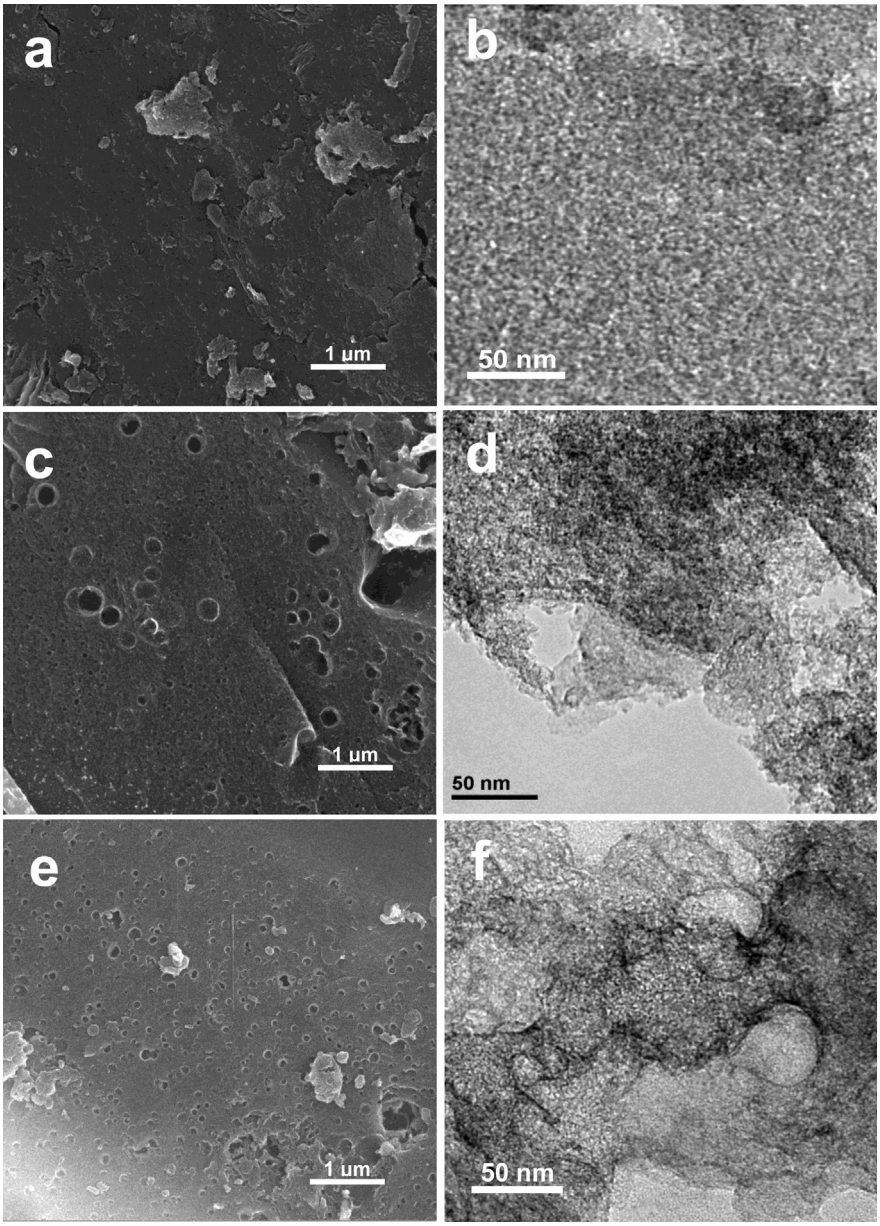

Fig. 1 – SEM (a, c and e) and TEM (b, d and f) images of the carbons: RC (a, b), AlRC (c, d) and SiRC (e, f).